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THE SOLUTION OF ELEMENTS IN THE MOLTEN SYSTEM $\text{AlCl}_3\text{-NaCl}$

V. O. Plotnikov and N. S. Fortunatov

Translation of "Rozchynennya elementiv u roztopleniy systemi $\text{AlCl}_3\text{-NaCl}$ ", Memoirs of the Institute of Chemistry, Academy of Sciences of the Ukrainian SSR, v. 3, 1936, pp. 123-128.



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16. Abstract The soly. of Hg, P, Mn, W, Mo, Cu, Si and S in molten 1:1 AlCl_3 - NaCl was measured at 150-370°. Except with S, there is no chem. reaction between the solutes and the solvent.			
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THE SOLUTION OF ELEMENTS IN THE MOLTEN

SYSTEM AlCl_3 -NaCl

by V. O. Plotnikov and N. S. Fortunatov

in Zapysky Instytutu Khemiy UAN, Academy of Sciences of the Ukrainian SSR, Kiev,
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The solution of metals in molten salts was studied early by R. Lorenz [Ref. 1]. This phenomenon is frequently observed in processes of electrolysis in molten salts. The so-called "metallic fog" is of crucial importance in a whole number of processes used in practice. Lorenz established the wide use of these phenomena but was unable to explain the nature of such solutions. He studied salts or melts in the solid cooled form. In this case the metals showed up in the crystalline state and dispersed. The intense color of the solutions, the phenomenon of opalescence, which is sometimes observed in these solutions, and a number of other properties were the reason that Lorenz used to apply the term "pyrozole" [term unknown] to these solutions, which points to their colloidal structure.

Subsequently, studies by Eutel [Ref. 2], Lange [Ref. 3], and Heyman [Ref. 4] established that dispersion is very high when metals are present in the melt. Finally, the work by Heyman and Friedlander [Ref. 5] established that cadmium in the molten cadmium-chloride system is in atomic solution.

As far as the solution of metals in salts and melts is concerned, three assumptions are made: (1) In dissolving, metals will yield compounds of lower valences, the so-called subcompounds; (2) In dissolving, metals will yield colloidal solutions; and (3) Metals will yield "true" solutions.

In our work with the AlCl_3 -NaCl system, we have found an exceptionally interesting phenomenon connected to the solution of the most diverse elements. The attached table of solutions we have studied will be expanded in the near future.

For some of these elements, we measured their solubility at several temperatures.

The measurements were performed as follows:

Using the equipment shown in Figure 1, aluminum-chloride was driven under vacuum from part A to part B in which baked sodium-chloride is placed ahead of time. Then the dams in the exits from vessel B are cooled, with sublimated aluminum-chloride collecting in them. The latter formed plugs, which prevented the aluminum-chloride vapors from spreading throughout the equipment. The mixture of aluminum-chloride and sodium-chloride was melted and poured into separate vessels C. These contained the materials to be dissolved. They were then fused shut and placed in a thermostatic furnace, kept there at the required temperature, shaken from time to time, with part of the melt poured into a separate appendage D after two hours, after which the melt was cooled down to solidification. The concentration of the melted substance was determined from analyzing the content of the sphere. In those cases where the dissolved substance was extracted as a powder, a glass filter E was fused into the small tube connecting C with the sphere D.

Results of the analysis are given in Table 2.

It should be noted here that the solubility of the substances studied is low and frequently decreases when temperature increases.

In order to clarify the nature of the melt -- whether dispersion in it is colloidal or molecular (whether the solution takes place at the expense of the well-known chemical interaction between the solvent and the substance to be dissolved) -- we made measurements whose essence was to determine the coefficient of distribution between molten and gaseous phases. Pressure was kept constant. This was done by using an elbow tube (Figure 2), one end of which was filled with AlCl_2 -NaCl, and

the other contained the substance to be dissolved. The tubes were evacuated during heating of the melt and fused shut. The end of the tube containing the melt was placed in a vapor heater using diphenyl-amine (boiling point, 302°C) so that all of the melt was inside the heater. The other end was placed in a vapor heater using naphthalene (boiling point, 218°C), methyl-salicylate (boiling point, 223°C), or diphenyl-amine. The intervening portion of the tube was heated by an electric wrap-around heater, so that no part of the tube was below the temperature of the second vapor heater. Under these conditions, the vapor of the substance had to diffuse through the entire connecting tube and dissolve in the melt. In order to establish equilibrium, the tubes were heated continuously for a duration of four to five days. Tests were made with sulphur and with mercury. The composition of the melt was: $\text{NaCl} : \text{AlCl}_3 = 48.3\% : 51.7\%$. Equilibrium results were determined by analysis.

The amount of sulphur does not seem to depend on the pressure of the vapor.

Thus, it apparently follows that, during the dissolving of sulphur, a chemical reaction takes place between it and the AlCl_3 ; this is also confirmed by the fact that in dissolving the sulphur melt in water there is always a smell of H_2S .

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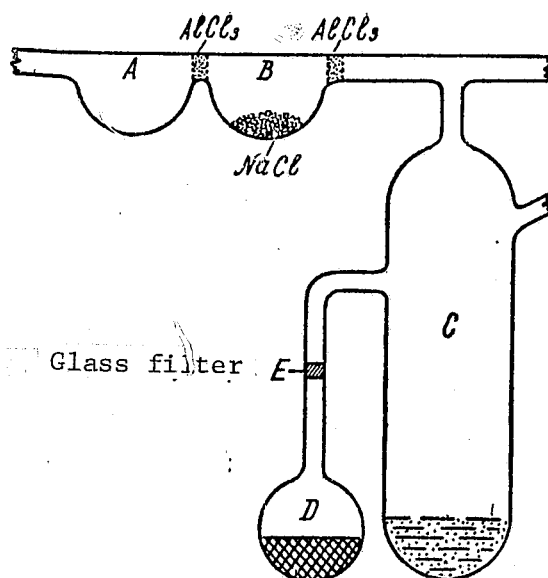


Figure 1.

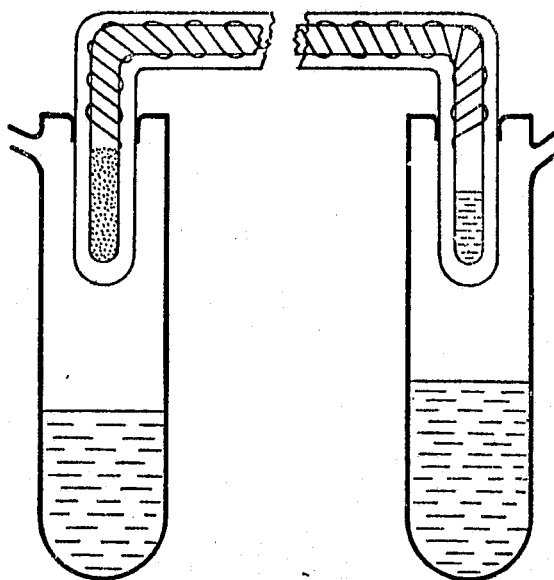


Figure 2.

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Table 1.

Element	Temperature of the Observed Solution (0°)	Color of the Solution
Boron	600 - 800	Green
Silicon	250 - 400	Gray
Tin	200 - 400	Orange
Lead	200 - 400	Brown
Phosphorus	140 - 400	Colorless or red
Arsenic	150 - 400	Slightly dark or yellow-brown
Stibium	150 - 400	Yellow-brown
Bismuth	150 - 400	Yellow-brown
Thallium	150 - 400	Dark
Sulphur	150 - 400	Yellow
Selenium	150 - 400	Dark brown
Tellurium	150 - 400	Dark yellow
Chromium	250 - 800	Lilac
Molybdenum	150 - 400	Orange-red
Tungsten	150 - 400	Orange
Manganese	150 - 400	Grayish
Iron	600 - 800	Dark
Mercury	140 - 400	Yellow to brown
Copper	300 - 600	From yellow to pink
Cadmium	150 - 400	Yellow
Silver	400 - 600	Dark
Gold	400 - 600	Brown
Platinum	250 - 400	Gray-brown
Palladium	250 - 400	Gray-brown

Table 1A. Results for Mercury

Temperature (0°)	P (in mm)	Percentage According to Analysis			Ratio Hg/p (in mm)
		1	2	3	
218	30.27	0.066	0.066	0.064	0.00218
223	35.11	0.074	0.078	0.076	0.00216
302	257.88	0.559	0.560	0.561	0.00217

Table 1B. Tests With Sulphur Yield

Temperature (0°)	P (in mm)	Amount of Sulphur %
218	4.1	2.16
223	5.0	2.12
302	50.4	2.20

Table 2.

Element	Temperature (°)	Concentration (%)	Method of Analysis
Mercury	268	0.880	Electrolysis using golden wire
	307	0.560	
	350	1.152	
Phosphorus	255	0.019	Precipitation using ammonium-molybdate
	294	0.786	
	350	1.60	
Manganese	150	0.011	Calorimetric
	350	0.009	
Tungsten	255	0.048	Precipitation
	290	0.091	
	320	0.122	
Molybdenum	256	0.253	Calorimetric
	318	0.166	
	350	0.157	
Copper	325	0.078	Calorimetric
	320	0.012	
	250	0.008	
Silicon	320	0.20	Oxidation and precipitation
	350	0.22	
	370	0.26	
Sulphur	206	1.34	Oxidation and precipitation
	223	1.34	
	307	2.23	

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